A water solution of this color is readily reduced by tin and hydrochloric acid, and reoxidized by ferric chloride. This at once eliminates all the azo dyes and magenta, which are by far the most common dyes used, and leaves only dyes of Class II of the scheme proposed by Rota.[1] All the coal-tar dyes used as archil substitutes and which resemble it in color are azo dyes, and can be readily distinguished from the archil color. If it is desired still farther to identify the color, it can be treated as described by Allen.[2] If it is found by the wool dyeing tests that some added color is present and that amyl alcohol extracts a reddish purple color from an ammoniacal solution, which is readily reduced by tin and hydrochloric acid and reoxidized by ferric chloride, we may be certain that the color is one of the lichen colors, archil, cudbear or litmus, all of which act in a similar way.

These colors are on the market in a number of different forms, as extracts or pastes, as ground-up lichens, or as sulphonated orceïne. This latter form might be readily mistaken for a coal-tar dye on account of its appearance and solubility, but it gives all the reactions of the non-sulphonated colors and can be identified as described above.

THE BASIC PROPERTIES AND THE QUADRIVALENCE OF OXYGEN.

By D. McIntosh.

Received October 18, 1904.

In a paper[3] on the basic properties of oxygen, Archibald and McIntosh, continuing the work on the chemistry of low temperatures begun by Walker, McIntosh and Archibald[4] have described additive compounds of organic substances containing oxygen with the halide acids, and have shown that the constitutions of these compounds can be satisfactorily represented by assuming oxygen to have a valency higher than two. Such a supposition was almost imperative in the case of the compounds investigated containing only hydrogen, carbon and oxygen, since

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[1] *Chem. Ztg.*, **22**, 437-442; 1898, U. S. Department of Agriculture, Bureau of Chemistry, Bull. 65, pp. 115-118.

[2] Vol. III, part 1, pp. 525 to 541.

[3] *J. Chem. Soc.* (London), **85**, 919 (1904).

[4] *Ibid.*, **85**, 1098 (1904).

hydrogen is looked upon as a monad, and experiments have as yet failed to show the existence of substances in which the valency of carbon exceeds four.

In some of the compounds described, such as those formed from liquefied hydrochloric acid and the ethers, the valency of the oxygen might even be assumed to be as high as twelve. But since hydrogen choride in contrast to hydrogen bromide and iodide polymerizes when liquefied, the valency of the chlorine might with equal justice be looked upon as rising from one to three, while the oxygen remains quadrivalent.

Archibald and McIntosh's collected results appear in the following table and indicate that as the temperature at which these bodies are stable decreases, the valency of the oxygen increases, but only in the case of the hydrogen chloride compounds is it greater than six. This result is of sufficient interest to warrant the investigation of a few more compounds of hydrogen iodide and bromide which seem likely to melt at a low temperature, and thus to show whether oxygen can exist under these conditions, with a valency of eight or twelve.

	Molecules of acid.	Molecules of organic liquid.	Melting-point.	Valency of oxygen.
HI	1	Acetone (2)	— 18°	4
	1	Ether (1)	— 18	4
	2	Propyl alcohol (1)	— 70	6
HBr	1	Acetone (1)	— 9	4
	1	Ether (1)	— 40	4
	2	Propyl alcohol (1)	— 85	6
HCl	5	Acetone (2)	— 85	8
	5	Ethyl ether (1)	— 92	12
	5	Methyl ether (1)	—120(?)	12
	5	Propyl alcohol (1)	—120(?)	12

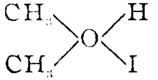
Of the ethers, the most likely for the purpose mentioned above was the most volatile one of the fatty series, dimethyl ether, boiling at —26° C.; an ether, too, of particular interest, on account of the work of Friedel, who predicted the influence of temperature on valency, and who was the pioneer in what may be called low temperature chemistry. The other body containing oxygen chosen as the most suitable was methyl alcohol.

The methods of preparation of the halogen acids and of the compounds are described in the paper previously referred to. The compounds were white, crystalline, almost insoluble[1] in the ether or alcohol, but quite soluble in the acid from which they were made, and in which they readily formed supersaturated solntions from which they could be precipitated by the addition of the solid phase. They had a sharp melting-point and their formation took place with the evolution of a large amount of heat.

The method of analysis was similar to that previously described. The body was dried in a jacketed filter-tube by means of air drawn through it, and it may be well to point out that the amount of acid found in such a compound will be invariably low. Indeed, it seems hardly possible to devise a method which will give results neither too low nor too high; for if the alcohol or ether is used to wash the body, some will be absorbed and the results will be low; if acid is used, it will be in excess and the results will be high. The alcohol or ether has, in all cases, been used for washing.

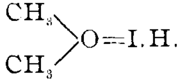
1. The compound of methyl ether and hydriodic acid melted at —15° C. The following are the results of the analyses (Preparation I was washed with a comparatively large amount of ether; Preparation II with very little): Preparation I gave 65.9, 66.9, 66.4; mean, 66.4 per cent. hydriodic acid. Preparation II gave 68.3, 69.6, 70.0; mean, 69.3 per cent. C_2H_6OHI requires 73.6 per cent. of acid, while $(C_2H_6O)_2HI$ requires 58.2 per cent.

The formula is therefore $C_2H_6O.HI$, and the constitution



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > O < \begin{matrix} H \\ I \end{matrix}$$

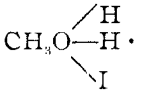
or



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > O = I.H.$$

That the former is the correct structural formula is almost certain, for in the case of diethyl ether dissolved in a halide acid, Dr. Steele[2] has shown that the ether moves to the cathode during electrolysis.

2. Methyl alcohol and hydriodic acid gave a compound melting at —48°. The analytical results are: I, 76.0, 78.4; II, 76.2, 75.6; mean, 76.5 per cent. hydriodic acid. CH_4OHI requires 80 per cent. acid. The constitution is therefore



$$CH_3O \begin{matrix} / H \\ — H \\ \backslash I \end{matrix} \cdot$$

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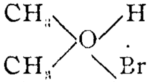
[1] While water is quite insoluble in either the halogen acid or the ether at low temperature, it is apparently much more soluble in some mixtures of the two.

[2] The account of this work is as yet unpublished, but Dr. Steele has kindly allowed me to make use of this result.

3. Methyl ether and hydrobromic acid. Melting-point, —22°. The analysis gave: I, 63.2, 64.2, 63.3; mean, 63.6. II, 63.2, 63.6, 63.3; mean, 63.3 per cent. hydrobromic acid. C_2H_6OHBr requires 63.8 per cent. of acid, and the constitution is therefore



4. Methyl alcohol and hydrobromic acid. Melting-point, —14°. The analysis gave: I, 67.8; II, 68.5, 68.6; mean, 68.3 per cent. hydrobromic acid. CH_4OHBr requires 71.7 per cent. of acid and the constitution is

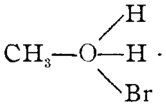


TABLE II.—COLLECTED RESULTS.

	Molecules of acid.	Molecules of organic liquid.	Melting-point.	Valency of oxygen.
HI	1	Ether (1)	—15°	4
	1	Alcohol (1)	—48	4
HBr	1	Ether (1)	—22	4
	1	Alcohol (1)	—14	4

In the above table the analytical results are collected and show the simplest proportion in which the bodies are formed and the temperatures at which they decompose (melt). The low melting-point of the compounds of alcohol with hydrogen iodide, as compared with the corresponding hydrogen bromide compound, is strange, but a similar anomaly was noticed with acetone (Table I). The oxygen is in all cases quadrivalent and from a comparison of the melting-points with those in Table I this is to be expected.

These compounds, therefore, are unsuitable for the purpose for which the research was undertaken and I can think of no bodies containing oxygen, which with hydrogen iodide[1] or bromide seem likely to give additive compounds melting at —90° or —100°. We must then, for the present, regard six as the highest valency of oxygen, a number which agrees perfectly with its position in the sixth column of the periodic table.

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October, 1904.

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[1] Other acids give additive compounds with organic bodies. With sulphuric acid: see Hoogewerff and W. A. Van Dorp, *Recueil. trav. chim. Pays-Bas*, **21**, 349 (1902); nitric acid probably acts like sulphuric, while chlorsulphonic acid gives a series of stable bodies with the ethers.